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Evaluation methods and research progresses in bio-oil storage stability

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ABSTRACT

Bio-oil is the liquid product of the fast pyrolysis of biomass. Recently, bio-oil has gained increasing attention for its direct use in combustion within boilers and furnaces as well as its use in automobiles and chemical materials after refining. Unfortunately, the composition of bio-oil is very complex. Aging occurs during storage, which leads to obvious changes in the physical and chemical properties of the oil. The poor storage stability of bio-oil restricts its extensive applications as a key renewable energy alternative. Viscosity and average molecular weight, as well as water and solid content can measured to determine changes in bio-oil. In this article, the testing parameters and technologies used for examining bio-oil stability and research progress in the field of bio-oil stability are reviewed. Emphasis is placed on thermal and oxidation stability. Scientific and technical developments towards improving bio-oil stability are also discussed. Furthermore, important aspects for consideration when developing experimental plans for bio-oil upgrades are examined. It also points out challenges to success with bio-oil upgrading in the future.

Contents

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1. Introduction

Biomass is the well known renewable energy resource which has advantages of being environmentally friendly, available in large reserves, and CO_2/green house gas neutral [1,2]. Fast pyrolysis of biomass is a thermo-chemical conversion process under anaerobic conditions at intermediate temperatures (about 500 °C) and produces liquid product (bio-oil), solid product (biochar), and gaseous product (fuel gas) [3]. It has been recognized as one of the most important methods for biomass utilization [4].

In recent years, fast pyrolysis of biomass for bio-oil production has received increasing attention [5,6]. Self-heating fast pyrolysis using straw as the raw material determined the yield and calorific values to be 50–55% and 15–16 MJ/kg for bio-oil and 28–33% and 18–20 MJ/kg for biochar, respectively; for forestry waste, bio-oil has a yield of 60–70% and calorific value of 16–17 MJ/kg, while biochar has a yield of 20–25% and calorific value of 20–22 MJ/kg, respectively [7,8]. Bio-oil is high in energy density, low in sulfur and nitrogen content, and is easy to store, transport, and utilize [2]. For these reasons, bio-oil is considered to be a clean fuel which can be directly used as fuel for combustion in boilers and furnaces [9]. Once it is refined, bio-oil can also be used as engine fuel and chemical materials [10–12]. In recent years, the prices of fossil fuel oils have risen with the increasing prices of crude oil. These increases have led to reduced oil resources of industrial burning oil. Hence, the market prospects of bio-oil obtained from the fast pyrolysis of biomass as fuel for industrial furnaces and oil burning boilers are promising [13]. From the long term perspectives, bio-oil has a broader market prospect as vehicle fuels or chemical materials to produce basic chemicals [14].

Although bio-oil is considered as a key renewable energy alternative, it has not been widely used due to some negative properties. First of all, there are hundreds of compounds in bio-oil and thus it is different to separate and refine [15]. Secondly, unlike fossil fuels, bio-oil exhibits characteristics such as high oxygen concentration, high moisture content, high viscosity, high acidity, and low calorific value. But most of all, the stability of bio-oil is very poor, which lead to obvious changes in physical and chemical properties of bio-oil [16], and difficult utilization of bio-oil in existing devices [17–19]. During storage, the aging of bio-oil not only deteriorates the quality of bio-oil but also influences the refining of bio-oil and its extracted chemicals [20–23]. In terms of combustion, an aging bio-oil will lead to more serious abrasion, corrosion, carbon accumulation and poor working performance of gas turbine. After long-term placement, the originally homogeneous bio-oil is even divided into two or three mutually insoluble components. In addition, bio-oil has low pH values and contains solid mixtures [24]. These qualities further deteriorate the stability of bio-oil. Hence, the properties of bio-oil, especially the storage stability, need to be researched and improved.

Storage stability of bio-oil is a crucial factor of bio-oil and it has a significant effect on bio-oil application. Recently, numerous studies have been carried out on bio-oil stability. These previous studies involved several important aspects: (i) parameters used for the evaluation of bio-oil stability, which include water content [25], viscosity [18], solid content [26] and average molecular weight [27]; (ii) evaluation methods for storage stability of bio-oil, which mainly include thermoanalysis technologies [28], Fourier transform infrared spectroscopy (FTIR) [29], and gas chromatography/mass spectrometry (GC/MS) [30]; (iii) aging mechanism of bio-oil [31]; and (iv) methods to improve bio-oil stability, including biomass drying [32], ash and char removing [33], adding solvent [34], emulsification [35], adding antioxidant [36], catalytic cracking [37], catalytic hydrogenation [38], and catalytic esterification [39]. These previous studies achieved remarkable advances in understanding the storage stability of bio-oil. However, the thermal and oxidation stability of bio-oil, especially the scientific and technical developments towards improving bio-oil stability, have not been fully reviewed. As far as we know, there is no review paper that focused on the storage stability of bio-oil reported in the literature in the last 10 years. Due to lots of newest paper published, summarizing these new papers and data is essential in order to better provide the information for the use of bio-oil.

Therefore, this paper reviews the research progress of bio-oil stability, with emphasis on thermal and oxidation stability. Additionally, methods for evaluation and technologies used for improvement of bio-oil are discussed. It also points out challenges to success with bio-oil upgrading in the future.

2. Basic properties of bio-oil

2.1. Physical properties

Bio-oil is a flowing liquid that is sepia in color, opaque, sticky and pungent. Table 1 shows the basic properties of bio-oil and fossil fuel [40]. Compared with fossil fuels, bio-oil has the

Table 1
Basic property of bio-oil and fossil fuel [20].

Fuel property	Bio-oil	Crude oil	Heavy fuel oil	Diesel	Gasoline
Water (%)	20～30	0.3	0.1	0.1	0.025
Solids /%	< 1		0.2～2.5	< 0.5	–
Ash (%)	0.1～0.5	0.02～0.07	> 0.3	< 0.01	–
C (%)	32～50	84～87	85～86	85～86	84～88
H (%)	8～11	11～14	12.5～14	13～15	12～16
N (%)	< 0.4	0.02～1.7	0.2	0.1	0.1
O (%)	45～60	0.08～1.82	1	–	–
S (%)	< 0.3	0.06～2	> 1	0.2～0.5	0.08
Stability	Unstable	–	Steady	Steady	Steady
Viscosity (cSt)	10～90 (40 °C)	20～40 (40 °C)	20～200 (80 °C)	1.6～5.8 (40 °C)	0.6～0.7 (40 °C)
Density (g mL^{-3})	1.2	0.7～1.0	< 0.98	0.85	0.7～0.8
Flash point (°C)	70～100	−10～28	< 130	40～55	−50～−40
HHV (MJ kg^{-1})	15～18	41～45	39～41	40～46	46
pH	2.0～4.0	–	–	––	–

characteristics of high oxygen concentration, high moisture content, high viscosity, high acidity, low calorific value and poor stability.

The oxygen concentration of bio-oil is typically 45–60% and is the root cause for the low calorific value of bio-oil. The calorific value of bio-oil produced from various raw materials is approximately 15–18 MJ/kg. The high oxygen concentration in bio-oil is a result of the oxygen content in the raw biomass materials. Luik et al. researched the pyrolysis of pine bark [41]. The results showed that 17–43% of the oxygen in biomass is converted into carbon dioxide. The remaining oxygen is converted into water and oxy-organics, both of which are ultimately present in the bio-oil. Thus, it is vital to control reaction conditions such that oxygen is primarily removed from biomass materials in the form of CO_2. This effort will subsequently lead to increases in the calorific value of bio-oil. Bio-oil contains a lot of water. The high water content (20–30%) reduces the viscosity, enhances mobility, and reduces the calorific value [7]. Excessively high moisture content can potentially cause phase-separate within the bio-oil. Bio-oil has a high viscosity that can change with fluctuations in moisture content and undissolved substances [28]. The corrosivity of bio-oil is a result of the substantial amounts of organic acids, such as formic, acetic, and propionic acids. These acids maintain bio-oil pH levels from 2.0 to 4.0. The acidity of bio-oil is 50–100 mg KOH/g. The significant corrosiveness of bio-oil also hinders its direct application in internal combustion engines.

2.2. Chemical properties

Composition of bio-oil is very complex. It contains hundreds of compounds, covering almost all types of oxygen-containing compounds like acids, alcohols, aldehydes, ketones, phenols, ethers, esters, sugars, aromatic hydrocarbons, as well as moisture and a small amount of solid particulate matters [15]. So far, over 300 kinds of components in bio-oil have been identified [9,42].

Previous studies have verified that 30–40% of bio-oil components can be detected by gas chromatography/mass spectrometry (GC/MS) [42,43]. Additionally, 15–25% of the volatile components can be measured using high performance liquid chromatography (HPLC) [15,44]. Approximately 25% of bio-oil components are high molecular weight substances that were found to be undetectable [8,45]. Quantification of some typical components in bio-oil detected by GC/MS and HPLC are shown in Table 2 [46,47].

Bio-oil is a pyrolysis product under non-thermodynamic equilibrium conditions. The components of bio-oil contain a large portion of unsaturated bonds (such as C=C, C=O, etc.). Compounds containing unsaturated bonds tend to undergo internal reactions during storage, such as polymerization, condensation, esterization, and oxidation. The content of these bonds and their downstream reactions are responsible for the poor storage and thermal stability of bio-oil [48].

Table 2
Quantitative concentrations of some typical components in bio-oil detected by GC/MS and HPLC (wt%).

Quantification method	Compound	Group	Typical wood [28]	Switch grass [29]
Cellulose/hemicellulose-derived compounds (wt%)				
HPLC	Acetic acid	Acids	0.5–12.0	2.94
HPLC	Glyoxal	Aldehyde	0.1–1.1	Trace
GC/MS	Furfural	Furan	0.1–1.1	0.62
GC/MS	Furfuryl alcohol	Furan	0.1–5.2	
GC/MS	2-Methyl-2-cyclopenten-1-one	Ketone		0.16
GC/MS	3-Methyl-2-cyclopenten-1-one	Ketone		0.34
HPLC	Hydroxyacetaldehyde	Oxygenates	0.9–13	2.40
GC/MS	4-Hydroxy-4-methyl-2-pentanone	Oxygenates		0.05
HPLC	Acetol	Oxygenates	0.7–7.4	2.75
HPLC	Levoglucosan	Sugar	4.8–5.4	6.38
Lignin-derived compounds (wt%)				
GC/MS	Guaiacol	Phenol	0.1–1.1	0.18
GC/MS	2-Methoxy-4-methylphenol	Phenol	0.1–1.9	0.07
GC/MS	Isoeugenol	Phenol	0.1–7.2	0.45
GC/MS	2,6-Dimethoxyphenol	Phenol	0.7–4.8	0.20
GC/MS	Phenol	Phenol	0.1–3.8	0.66
GC/MS	*o*-Cresol	Phenol	0.1–0.6	0.19
GC/MS	2,5-Dimethylphenol	Phenol		0.01
GC/MS	*p*-Cresol	Phenol	0.1–0.5	0.27
GC/MS	*m*-Cresol	Phenol	0.1–0.4	0.20
GC/MS	2,4-Dimethylphenol	Phenol	0.1–0.3	0.10
GC/MS	3,5-Dimethylphenol	Phenol		0.05
GC/MS	4-Ethylphenol	Phenol		0.22
GC/MS	3-Ethylphenol	Phenol		0.04
GC/MS	2-Ethylphenol	Phenol	0.1–1.3	0.03

3. Evaluation of bio-oil storage stability

3.1. Evaluation parameters

Bio-oil storage stability refers to its ability to maintain the original physical and chemical properties during storage in various environments and conditions. Physical and chemical properties of traditional fossil fuels will not change during the storage, transportation and utilization but bio-oil is hard to maintain the stability. This section will discuss various parameters used for the evaluation of bio-oil stability. These parameters include water content [25], viscosity [18], solid content [26] and average molecular weight [27].

3.1.1. Water content

The majority of water in bio-oil is from free water in the raw materials and the dehydration reaction during pyrolysis [49]. Therefore, bio-oil inevitably contains high levels of water. During bio-oil storage, aging reactions also generate water [50]. Generally, phase separation occurs when the water content in bio-oil is higher than 30%. Since bio-oil contains many organic substances with low molecular weights, traditional drying method are not appropriate for measuring water content. Instead, it is commonly measured using the Karl Fischer titrimetric method [51,52]. Before the testing, the bio-oil must be shaken to ensure the water content is consistent throughout the sample.

3.1.2. Viscosity

The viscosity of homogeneous bio-oil can be measured as either dynamic or kinematic viscosity by using different viscometers, such as capillary and falling ball viscometers [7,53,54]. Changes in the viscosity of bio-oil can intuitively reflect changes in the bio-oil's physical and/or chemical properties. The viscosity of bio-oil is primarily determined by its composition [55,56]. The viscosity of bio-oil decreases with higher contents of water and low molecular weight compounds while it increases with higher contents of lignin pyrolysis materials and insoluble solids.

Bio-oil viscosity also decreases as the temperature increases [28]. Below 80 °C, its logarithm shows linear increases with rising temperatures, which is in accordance with the properties of Newtonian fluids. [34] However, when exceeding 80 °C, some substances within the oil volatilize and polymerization may occur, causing inaccurate measurements. Therefore, the viscosity should be measured at the temperature no more than 80 °C [57]. Oasmaa et al. conducted substantial verifications of analytical standards of

physical and chemical properties of bio-oil, and they found that the measurement at 40 °C effectively minimized systematic errors [53].

3.1.3. Solid

The solid content in bio-oil is less than l wt% [2]. These solids consist of incompletely separated coke formed during biomass pyrolysis, impurities in the biomass (e.g. dust), and impurities attained during collection and storage. General heavy oil boilers have no strict requirements for solid content, thus bio-oil can be used for this application easily. However, the high precision requirements of diesel fuel injection systems can become worn by the particulates in bio-oil, so use of bio-oil in this application is restricted [9]. Therefore, solid content in bio-oil should be minimized since these particulates can also act as catalysts and accelerate the aging process [58].

Solid content of bio-oil is measure med by mixing 10 g of bio-oil with 100 mL organic solvents. The mixture is then repeatedly filtered using 1 μm pore size filter paper until the filtrate becomes clear. The filter paper and residues are dried for 15 min at room temperature followed by 30 min at 150 °C. The amount of solid particles can then be calculated by weighing the residues and the initial weight of the bio-oil [59]. The solubility of bio-oil is dependent on the organic solvent used. Systematic studies conducted by VTT recommended to use ethanol for bio-oil derived from hardwood, cork, and straw; and to use mixtures of methylene chloride and methanol for bio-oil derived from forestry waste and tree bark. [60]. Quantitative distribution and particle size distribution of solid in bio-oil can be also be effectively measured by microscope or scanning electron [61].

3.1.4. Average molecular weight

Variations in the average molecular weight of bio-oil can directly affect the aging process. When in storage, low molecular weight compounds within bio-oil can polymerize and create oligomers with higher molecular weight [20,62]. The main methods for measuring molecular weight distribution are electrospray ionization mass spectrometry (ESI-MS), size exclusion chromatography (SEC), molecular beam mass spectrometry (MBMS), gel permeation chromatography (GPC), etc. [27].

Compositions in bio-oil are complex and the range of molecular weights is also very wide. According to the measurement results of Perez, most molecular weights in bio-oil were below 10,000 g/mol and two peak values occurred at 100 g/mol and 700 g/mol [63]. In other words, molecules in the two molecular weight ranges were relatively concentrated. After the aging, molecular weights below 1000 g/mol were reduced while molecular weights over 1000 g/mol increased significantly.

3.2. Evaluation methods

The storage stability of bio-oil is typically assessed using thermoanalysis technologies, Fourier transform infrared spectroscopy (FTIR) and gas chromatography/mass spectrometry (GC/MS).

3.2.1. Thermoanalysis technologies

Thermoanalysis technologies, such as thermalgravimetric analysis (TGA) and differential scanning calorimetry (DSC), are important methods when assessing the storage stability of bio-oil. From TGA, the relationship between bio-oil weight loss and temperature in an inert atmosphere can be obtained [64,65]. Generally, if the sample weight loss peak corresponds to a higher temperature, the thermal stability is better. For oxidative stability, previous studies have shown that DSC is an effective method that can be used to assess the oxidative stability of bio-oil [28,66,67]. This experimental process is according to the standard method of using DSC to assess the oxidative stability of antioxidant (ASTM E2009, ASTM D5483). In brief, during the temperature programming under air condition, bio-oil will have exothermic reaction when reaching certain temperature. The initial oxidative temperature of samples can be measured by extrapolation. Higher initial oxidative temperature indicates better oxidation stability [50].

Thermoanalysis technologies have many advantages, such as short experimental time, high accuracy, high sensitivity, and low sample requirement [32,68,69]. Although using fewer samples is advantageous, it does require highly on the homogeneous sampling and the operation precision.

3.2.2. FTIR

FTIR is widely used in the detection of organic functional groups [70]. FTIR can conveniently analyze functional groups of bio-oil under different storage conditions and infer the aging mechanism of bio-oil [71].

FTIR can be easily operated with low cost and less amounts of experimental samples required. However, strong absorption peaks formed from the moisture in bio-oil will affect the test [29]. Besides, the complexity of bio-oil components enhances the difficulties of precisely interpreting the fingerprint region of FTIR spectra [59]. Therefore, FTIR is commonly used as a complementary means to study the aging mechanism of bio-oil.

3.2.3. GC/MS

GC/MS has been widely used for composition analysis of bio-oil [72]. This method is capable of measuring changes in composition that occur during storage. This information can then be used to advance research on the aging of bio-oil [30].

The properties and components of bio-oil are determined by the materials used, pyrolysis conditions, pretreatment, and catalysts [73,74]. As a result, measurements taken via GC/MS differ within literature. For example, 12 European laboratories simultaneously analyzed and compared the physico-chemical properties of the same bio-oil samples [53,75]. The results showed that the quantitative analysis of chemical components in bio-oil measured in different laboratories varied greatly. Thus, it was recommended that standard samples should be used when making these measurements so that the quantitative accuracy can be improved. A great deal of experimental work and method modifications was previously required to reach accurate and consistent results from different laboratories.

3.2.4. Other technologies

Due to the complexity of bio-oil, bio-oil separation technology has also been extensively studied. These separation technologies include distillation [76,77], extraction [78,79], column chromatography [30,80], membrane separation [81,82], etc. Several research groups have analyzed the physicochemical properties of the different separated components in bio-oil, but limited research has been performed on the stability of this bio-oil.

4. Storage stability of bio-oil

4.1. Aging reaction mechanism

Bio-oil is composed of both polar and non-polar components [83]. At first, the polarity between different components is not very different. There are also some components both with low-polarity parts (long carbon hydrogen chains) and high-polarity parts (alcohol groups at the chain end), which helps promote their mutual solubility. Therefore bio-oil acts as a one-phase liquid. However, the polarity of bio-oil is changed due to storage

temperature, storage time, light, oxygen, and chemical reactions. For example, esterification converts highly-polar organic acids and alcohols to low-polarity esters and highly-polar water. In this way, the polarity differential within bio-oil expands and the possibility for phase separation increases [68,84,85].

Although the changes in physical properties during aging have been well characterized, a precise and detailed conclusion has not been reached with regard to changes in chemical properties [50,86]. Based on theoretical backgrounds, the main reactions responsible for bio-oil aging were found, for example, (a) esterification reactions that alcohols with organic acids forming esters and water, (b) transesterification reactions that exchanging of alcohol and acid groups in a mixture of two or more esters, (c) homopolymerization reactions that aldehydes reacting with each other to form polyacetal oligomers and polymers, (d) hydration reactions that aldehydes or ketones mixed with water react to form hydrates, (e) hemiacetal formation reactions that alcohol mixed with an aldehyde and then forming hemiacetal with a significant amount of heat liberating, (f) acetalization reactions that aldehydes and alcohols reacting to form acetals, and (g) phenol/aldehyde reactions and resins that phenol reacting as an alcohol with formaldehyde to form the hemiformal in the absence of catalysts, or, phenols and substituted phenols reacting with aldehyde hydrates to form novolak resins and water, as shown in Fig. 1 [17].

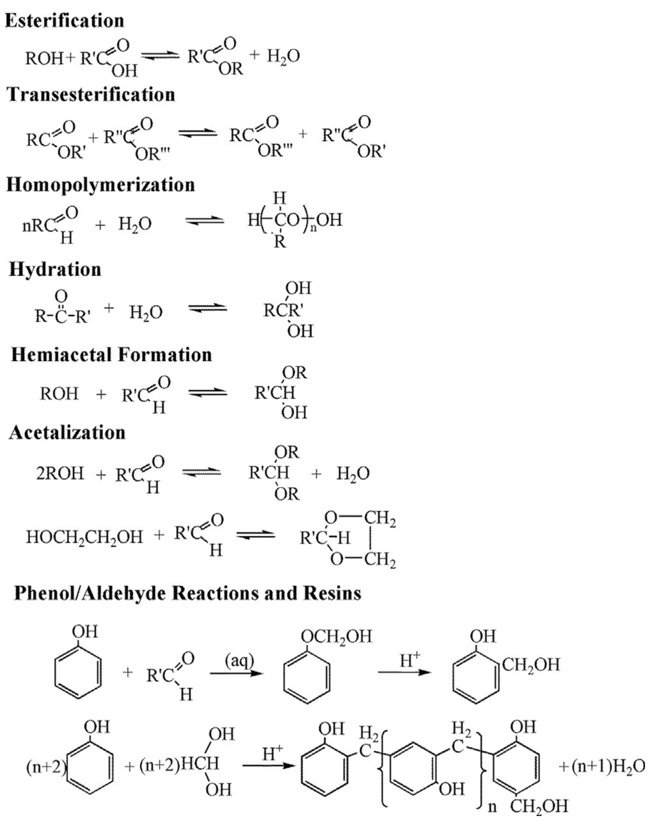


Fig. 1. The main chemical reactions responsible for bio-oil aging [17].

Xiong et al. carefully compared GC–MS spectra before and after bio-oil aging and found significant changes in many of the components [71]. They surveyed multiple potential aging reactions suggested in the literature [31], and proposed the scheme 1 of polymerization reactions between aromatic compounds and sugar compounds (Fig. 2) and the scheme 2 of reactions in aliphatic compounds (Fig. 3) [71].

It is also interesting to note that the pH of bio-oil before and after aging is basically unchanged, ranging from 2.9 to 3.0 [71]. This consistency indicates that there is no increase in acid during the aging process. Similar results were obtained by Oasmaa et al. [87], Hilten et al. [28], and Elliott et al. [18]. In the study of Oasmaa et al. [87], the amount of volatile carboxylic acids (C < 6) in bio-oils did not change significantly during storage at or below room

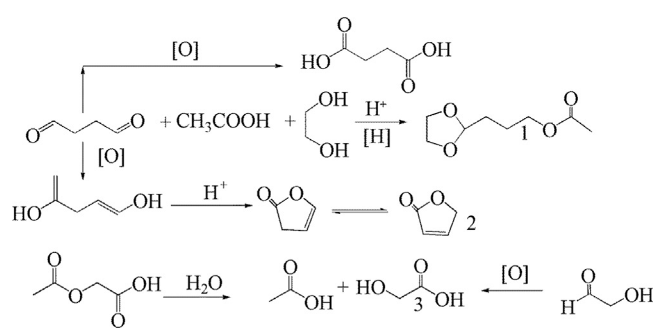


Fig. 3. The reactions of aliphatic compounds during the aging [62].

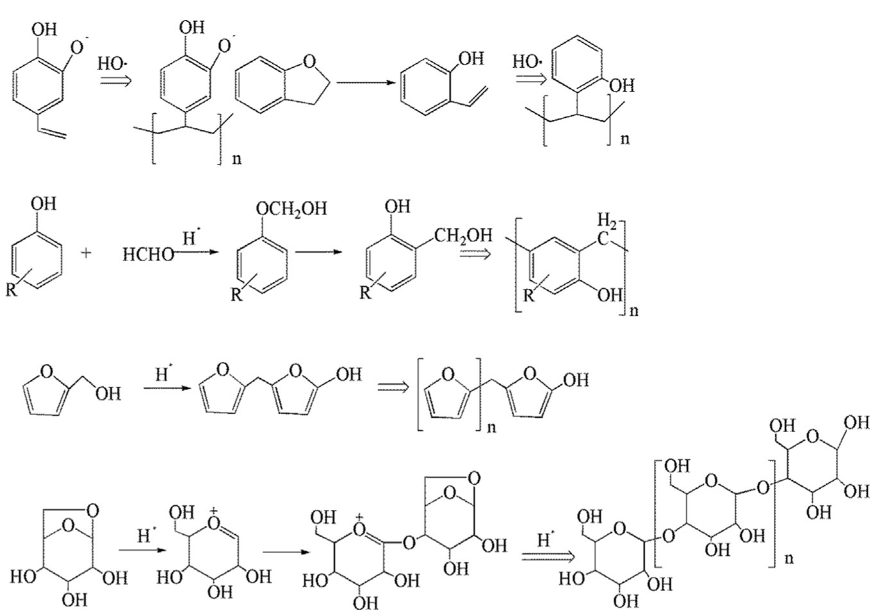


Fig. 2. The polymerization reaction of aromatic compounds and sugar compounds [62].

temperature, and that the concentration of acetic and formic acids also did not change during the stability test at 80 °C for 24 h, and thus it is quite clear that total acid number has no meaning in following the storage stability of bio-oils.

Currently, studies on storage stability of bio-oil are mainly conducted from two perspectives, namely, thermal stability and oxidative stability.

4.2. Thermal stability

Thermal stability refers to the ability of bio-oil to retain its original properties in a relatively high temperature environment. For bio-oil thermal stability research, accelerated aging experiments are generally used to analyze changes in the physicochemical properties of bio-oil [28]. Numerous studies have shown that in long-term storage process, viscosity, moisture content and average molecular weight of bio-oil were significantly affected by storage time and storage temperature [20–23,71]. The thermal stability of bio-oil gained attention as early as 1994 by Czernik et al. [88]. In their study, the average molecular weight change of bio-oil in storage was successfully fitted using first-order kinetics. The viscosity and average molecular weight of bio-oil were linearly correlated with the storage time under the storage conditions which were three-months at room temperature or 9 days at 60 °C. Oasmaa et al. investigated the one-year storage stability of 7 types of bio-oils [20]. Their results showed that the increase in viscosity after heating bio-oil to 80 °C for 24 h was equivalent to storing the same bio-oil at room temperature for one year. The increase in viscosity after 6 h at 80 °C or 1 week at 40 °C was similar to that of 3–4 months at room temperature. They also found that the water-soluble and ether-soluble components of bio-oil decreased with increasing of storage times, while the high-molecular weight pyrolytic lignin constantly increased. Similar results of bio-oil properties were observed by Lu et al. [34]. They found that the viscosity and moisture of bio-oil after 120 h of storage at 50 °C increased by 31.7% and 2.46%, respectively. And after 48 h of bio-oil aging at 80 °C, a slight phase separation occurred, and the viscosity and moisture increase reached 87.3% (viscosity at 40 °C) and 11.1%, respectively. However, after continuing aging for 72 h at 80 °C, serious phase separation happened and the viscosity and moisture could not be measured.

The changes in molecular weight can also intuitively describe the aging of bio-oil, as polymerization and condensation reactions occur between small molecules or between small molecules and oligomers in bio-oil. Chaala et al. found that after storing for 6 months at room temperature, the amount of compounds with a molecular weight lower than 400 decreased by 7.9 wt%, while the amount of compounds with a molecular weight higher than 500 increased by 7.8 wt% [50]. Perez et al. pointed out that after the aging of bio-oil, the number of molecules below 1000 g/mol reduced, while the number of molecules higher than 1000 g/mol increased obviously [63]. In addition, Fahmi et al. found that inorganic substance in bio-oil also have an effect on moisture content and molecular weight, and increase the possibility of phase separation of bio-oil [48].

Thermal analyzers are also an important means to analyze bio-oil thermal stability. Chaala et al. conducted TG experiments of the upper and bottom layers of bio-oil [50]. After storing at 80 °C for 168 h, the weight loss peak temperature of bottom layer bio-oil increased 56 °C compared with that of fresh bio-oil. The upper bio-oil did not change significantly. Guo et al. conducted TG-DTA analysis of bio-oil, and they found that the quality and thermal stability of bio-oil was greatly improved after the oil was refined [89]. Similar conclusions were obtained by Jiang et al. [35,90].

In addition to the accelerated aging and thermal analysis, the microstructure of bio-oil also can reveal aging behaviors. Ba et al. researched the thermal stability of bio-oil via microscopy and rheology [30,69]. Experimental results showed that bio-oil is a multiphase complex colloidal system consisting of solid particles, three-dimensional structures, and droplets. At low temperature (< 50 °C), the microstructures (e.g., waxy materials) in the bio-oil matrix are responsible for the high-viscosity. Garcìa-Pèrez et al. found that aging reactions formed both high-molecular compounds with a networked structure [63]. This structure is initially maintained by physical bonds, but increases in strength with the progressive formation of covalent bonds. The creation of such a network structure causes separation of some organic polar compounds and water, thus forming an aqueous phase. Meanwhile, the high-molecular compounds with reduced polarity remained in the oily phase at the bottom of bio-oil.

4.3. Oxidative stability

Oxidative stability refers to the ability of bio-oil to resist atmospheric (or oxygen) oxidation and to maintain the natural properties of bio-oil. As the oxidizing reaction of bio-oil is a complex mechanism, existing studies on the oxidative stability of bio-oil are still in their infancy. Oxygen and organic matters in bio-oil tend to form superoxides [59]. Superoxides can catalyze the polymerization of other substances such that the polarity differences within bio-oil substituents are enhanced. Hence, air-free technique can decrease the pace of aging to a certain extent. To demonstrate this, Xiong et al. conducted aging experiments of bio-oil under air and argon for 24 h. Their results showed that the water content of argon-protected bio-oil increased slightly, while bio-oil exposed to an air environment increased significantly [71]. After 12 h of oxygen-assisted aging, bio-oil showed obvious delamination. There were also approximately 70% pitch-shaped thickening matters on the bottom. Hilten et al. noted that the initial oxidizing temperature and oxidative stability of pine bio-oil were both higher than those of peanut shells bio-oil [28]. The authors also noted that the addition of organic solvents not only reduced particulate matters, but also promoted the oxidative stability of bio-oil. Garcìa-Pèrez et al. analyzed the oxidative stability of emulsified oil (bio-oil/biodiesel) using DSC [66]. The results showed that the initial oxidizing temperature of the bio-oil/biodiesel increased when more bio-oil was emulsified.

5. Methods to improve bio-oil stability

According to physical and chemical properties as well as the aging mechanisms of bio-oil during storage, various methods have been proposed to improve bio-oil stability.

5.1. Physical methods

5.1.1. Biomass drying

As previously mentioned, biomass materials often have a high content of moisture. This moisture will be transferred into bio-oil during the condensation portion of pyrolysis [91]. In addition to this, a considerable amount of water will be produced in the pyrolysis process. When the water content of bio-oil exceeds a certain limit (30%), phase separation usually occurs. Therefore, a drying pretreatment of biomass is essential for reduction of the water content to an acceptable level (< 10%). In recent years, the heat and mass transfer characteristics of biomass drying under isothermal and non-isothermal conditions have been well investigated [92–94]. In some pyrolysis liquefaction plants, pyrolysis gas or high temperature flue gas is used to dry biomass materials.

5.1.2. Ash and char removing

Biomass contains a large quantity of ash, especially in rice husk. The most common inorganic elements found in ash include potassium, calcium, sodium, magnesium, silicon, phosphorus and chlorine etc. Alkali metals (potassium and sodium) and alkaline-earth metals (calcium and magnesium) will catalyze the secondary reactions in biomass pyrolysis. This catalysis then reduces the productivity of bio-oil [95]. Besides, some tiny char particles also enter into bio-oil [26]. These particulate solid comprise the “condensation core” in the ageing process of bio-oil. Thus, the removal of ash, char, and especially metallic ions is vital to improving the stability of bio-oil. The currently adopted methods for completing these tasks include acid pickling, gas filtration, and liquid filtration.

(1) Dilute acid pretreatment of biomass
A significant amount of metal ions in biomass ash can be removed by performing dilute acid pretreatment before biomass pyrolysis, which would change the biomass thermal cracking reaction and possible increase some high value-added products in bio-oil [96]. Previous studies have shown that acid pretreatment significantly promotes small molecular products, furfural and phenol formation, and also lowers the productivity of complex phenolics [97]. Therefore, acid pretreatment can promote the gathering of some chemical products and improve the quality of bio-oil [33].
However, it has been demonstrated that acid pickling is not very effective in improving the bio-oil stability. Das et al. researched the impact of de-ashing bagasse on the yield and quality of bio-oil [98]. Results showed that the yield of bio-oil increased, but the stability was not improved because the acid and polar components of the bio-oil also increased. Moreover, it was also shown that pretreatment with acid also reduced the pyrolysis degree of lignin, thus increasing the macromolecule derivates of less soluble lignin in bio-oil. This treatment is harmful for the storage and utilization of bio-oil. In addition, after acid (water) leaching, biomass must be dried before pyrolysis, increasing the overall cost of pyrolysis.

(2) Hot gas filtration of pyrolysis vapors
Common cyclone separators can only remove particles larger than 10 μm. In order to obtain more pure bio-oil, the direct filtering of pyrolysis gases prior to condensation was proposed. Pyrolysis vapors filter performed normally when using materials like sintered metal and porous ceramic. Agblevor et al. adopted the 2 μm stainless steel filter and using such also found that the alkali metal concentration in bio-oil significantly decreased. In example, the potassium concentration was reduced from 300 mg/L to less than 10 mg/L [99]. Hoekstra et al. found that the size of solid particulate matters in bio-oil can be reduced to submicron level when wire gauze filter with the pore size of 2 μm was used [100]. Diebold et al. found that there was less than 10 mg/L of alkali concentration in bio-oil, and the increase rate of viscosity in storage was about one third of the unfiltered bio-oil [101]. Similar results were reported by Oasmaa and Peacocke [60]. It was found that after hot gas filtration, the pyrolysis liquids contained low ash contents (0.01 wt%) due to efficient removal of char fines with alkali (Na, K, Ca, Mg) metals (below 10 ppm). Chen et al. studied the effect of hot vapor filtration on the characterization of bio-oil from rice husks [102]. The results showed that the filtrated bio-oil had a lower yield, higher water content, higher pH, and lower alkali metal content. The kinetic viscosities of bio-oils from the condenser were 1.46 mm^2/s and 1.04 mm^2/s without and with hot vapor filtration, respectively. According to the above-mentioned studies, there are several drawbacks to this hot gas filtration method. These drawbacks include expensive filter materials, filter abrasion, and char cake accumulation. The major problem is the strict control of filtration temperature [103]. A lower temperature will lead to the condensation of pyrolysis gas on device surface, which will clog the filtering pore and increase the resistance. A higher temperature will lead to the secondary pyrolysis of pyrolysis gas with coke on the filter surface, thereby reducing the yield of bio-oil. In addition, the high-temperature filtration device needs a reliable blowback system or cleaning method in order to avoid excessive resistance of filters in long-term operation.

(3) Filtration of bio-oil
Elliott et al. made an attempt to separate tiny coke in bio-oil by liquid filtration technology. This attempt was unsuccessful due to the tendency of the oil drops to gather around particles of coke [104]. This not only led to excessive filtering resistance, but also caused substantial bio-oil loss. Similar experiments were carried out in our laboratory. We also found a great amount of bio-oil attached to the surface of filter net. Thus, based on the existing technologies, it is more effective to remove particles as much as possible before pyrolysis gas condensation.

5.1.3. Adding solvent

Adding mutually soluble organic solvents with bio-oil is the simplest and most effective method for the improvement of bio-oil stability. Diebold et al. studied the influence of different additives (e.g., ethyl acetate, methanol, acetone, ethanol) on the viscosity and stability of bio-oil [105]. Experimental results demonstrated that methanol was the most effective additive. Bio-oil containing 10% methanol can be stored steadily for 96 h at 90 °C. However, without the addition of methanol, the viscosity of bio-oil increased three times after being stored for 26 h. Lu et al. found that for bio-oil aged for 120 h at 50 °C, after the addition of 5 wt%, 10 wt% and 15 wt% methanol, the increase rate of viscosity dropped from 31.7% to 21.7%, 16.3% and 11.9% respectively, and the increase rate of moisture content dropped from 2.46% to 1.88%, 1.42% and 1.34% [34].

Solvents added to bio-oil influence the viscosity of bio-oil primarily by the following 3 types of mechanisms: (1) physical dilution; (2) reducing reactant concentration or changing microstructure of bio-oil to reduce the reaction rate; and (3) formation of an ester or acetal based on reacting with active components in bio-oil in order to prevent the generation of macromolecule polymer [2,22]. The addition of methanol reduces bio-oil viscosity, inhibits the aging and improves the stability of bio-oil. Nevertheless, only addition of solvents cannot essentially improve the quality of bio-oil. The high oxygen content, high moisture, low combustion performance of bio-oil are not been solved.

5.1.4. Emulsification

Bio-oil cannot be dissolved into non-polar hydrocarbon fuels like diesel. The addition of surfactants can change the surface properties of bio-oil and diesels to gain homogeneous mixed liquors. Chiaramonti et al. conducted the emulsification of the bio-oil and diesels mixed to different ratios [106,107]. The experiments involved about 100 kinds of surfactants, including cationic, anionic, and nonionic surfactants. The results showed that the higher the surfactant concentration, the more stable the emulsified oil. The optimal concentration of surfactant was found to be 0.5–2%. The authors also mentioned that the choice of appropriate emulsifier is very difficult, sometimes only relying on experience, due to the complexity of bio-oil composition. Ikura et al. found that bio-oil concentration, surfactant concentration, and input energy are three primary factors that influence the stability of

emulsified oil. These authors also found that the concentration of suitable emulgator is about 0.8–1.5% and the appropriate bio-oil concentration is 10–20% [108]. The reduction in viscosity and corrosively of the emulsion was also reported by Jiang et al. [35]. Currently studies have shown that emulsified oil of bio-oil and diesel can be used in the diesel engine [2,11]. The acidity and viscosity of emulsified oil are improved compared with original bio-oil. Also, the emission of particulate matters in combustion is greatly reduced.

Despite the recent advances in the field, some drawbacks are also found in the current emulsification technologies and applications: (1) the high cost of emulsified oil mainly stems from the costs of surfactant and energy input in emulsification; (2) emulsified oil seriously corrodes the engine; and (3) viscosity of emulsified oil is generally higher than diesels, which cannot meet some requirements of the internal combustion engine [11,109].

5.1.5. Adding antioxidant

As previously discussed, when bio-oil is exposed to the air, some active ingredients react with oxygen to produce peroxide. These peroxides catalyze the polymerization of olefins. Therefore, exposure to air should be avoided as much as possible during the storage, transfer, and processing of bio-oil. If possible, antioxidants should be added to the oil [36]. Many phenols can capture free radicals that catalyze the polymerization of olefins. However, the concentration of phenols in bio-oil is too low to ensure bio-oil stability. Phenols can be added to the mixture to aid in the stability process. Hydroquinone is often added for storage and transportation of bio-oil. This compound has been shown to stabilize acrolein [17]. It is more economical to use small amounts of antioxidants, such as hydroquinone, to stabilize olefins in bio-oil compared with catalytic hydrogenation for olefin saturation.

5.2. Chemical methods

Chemical refining can improve the stability of bio-oil. The primary methods for refining bio-oil include catalytic cracking, catalytic hydrogenation, and catalytic esterification. The core technology of all chemical refining methods is the selection of catalysts.

5.2.1. Catalytic cracking

Catalytic cracking is the process in which bio-oil or pyrolysis gas was further decomposed to smaller molecules via catalysis. Oxygen can be removed in forms of H_2O, CO and CO_2. Since the 1990s, traditional zeolites catalysts, such as HZSM-5 and HY, have been used for deep catalytic deoxidation of bio-oil or pyrolysis gas [37,110]. These catalysts possess a highly efficient deoxygenation feature and can generate liquid-state hydrocarbon products with aromatic hydrocarbon as the main product. Scholze et al. used manganese oxide as catalysts [111]. The results indicated that bio-oil has a high calorific value and less water content. Also, they discovered that a low level of viscosity can still be maintained during the storage at 80 °C. Nokkosmaki et al. compared the stability of refined bio-oil (from ZnO catalytic pyrolysis) and original bio-oil [112]. After storing for 24 h at 80 °C, the viscosity of refined bio-oil increased by 55% while that of the original bio-oil increased by 129%. Zhou et al. also found that zinc oxide could obviously decrease bio-oil's viscosity [113].

Catalytic pyrolysis also has some drawbacks, including a low yield of bio-oil, H elements lost, and catalyst deactivation. Based on the existing research conditions, the key to improving bio-oil stability via catalytic pyrolysis is finding to find a catalyst with high selectivity selectivity, high conversion, rate and low coking rate.

5.2.2. Catalytic hydrogenation

Catalytic hydrogenation involves various reactions, such as hydrogenation and deoxygenation, under high pressures and in the presence of hydrogen. Oxygen is removed in forms of H_2O and CO_2, thus obtaining liquid fuel with a high level of hydrocarbon, higher calorific value and good stability [114]. Compared with catalytic pyrolysis, the costs of catalytic hydrogenation are significantly higher. The reaction conditions of catalytic hydrogenation are very strict. Also, a great amount of hydrogen will be consumed. The complete deoxygenation of per kilogram of bio-oil needs to consume 600–1000 L of hydrogen.

Effective catalysts for the hydrogenation of bio-oil require not only high catalytic activity but also a long catalyst life [115]. In order to reduce cost and extend catalyst life, the catalytic hydrogenation of bio-oil is generally divided into two steps [38,116]. Firstly, at a relatively low reaction temperature, gentle, catalytic hydrogenation of bio-oil is carried out (<300 °C) to remove some components with poor stability (ketones, carboxylic acid esters, carboxylic acid and guaiacol). Next, conventional hydrogenation conditions are used for deeply deoxygenation (350–400 °C). The synchronization between the two stages is crucial in bio-oil catalytic hydrogenation. Various catalysts were applied to realize the gentle catalytic hydrogenation or deep hydrogenation. These catalysts include Ru/γ-Al_2O_3, commercial Ni-Mo/γ-Al_2O_3, Co-Mo/γ-Al_2O_3 or Co-Mo-P/γ-Al_2O_3, homogeneous $RuCl_2$ $(PPh_3)_3$, HZSM-5, Pd/SO_4^{2-}/ZrO_2/SBA-15, Pt/Al_2O_3, etc.

After catalytic hydrogenation, the bio-oil stability is improved. However, the current catalysts are all high-temperature catalysts while bio-oil thermal stability is poor. Therefore, the research and development of low-temperature and highly active catalysts is the key in bio-oil hydrogenation [117].

5.2.3. Catalytic esterification

Catalytic esterification can convert components in bio-oil, like carboxyl groups, by adding alcohol auxiliaries in bio-oil. This process thereby reduces the acidity of bio-oil and improves the stability of bio-oil. Common catalysts include solid acid catalyst. [118], solid alkali catalyst [119] and ionic liquid catalyst [39], etc. Zhang et al. demonstrated the use of solid acid catalysts [120]. Their results indicated that upon addition of the catalyst, the concentration of esters increased greatly and the stability of bio-oil was greatly improved. Meanwhile, the density of bio-oil decreased from 1.24 g/cm^3 to 0.96 g/cm^3 and the calorific value increased by about 50%. Additionally, the pH of bio-oil decreased from 2.60 to 1.12. Conversely, when a solid base catalyst was used, the pH increased to 5.93. Xiong et al. used ionic liquid catalysts to catalyze bio-oil [39]. The major improvements that the refinement of bio-oil enables are greater removal of acid and water. Meanwhile, as pyrolysis lignin was removed, the refined bio-oil had a much lower viscosity.

Unfortunately, the esterification reaction generally consumes a high amount of alcohol additives and can only process carboxylic acid. Moreover, the water produced in the esterification reaction also imposed adverse impacts on bio-oil stability. Currently, many researchers are working on the development of multi-functional catalysts. These catalysts will realize the gentle catalytic hydrogenation and catalytic esterification of bio-oil at the same time simultaneously.

6. Solution selections

Above all, the above-mentioned methods to improve storage stability of bio-oil show good effect, but the disadvantages are also obvious. Different methods can be taken into account at the same time to improve the storage stability of bio-oil. When developing

an experimental plan for bio-oil upgrading, the following aspects also should be considered:

(1) Mechanism of fast pyrolysis of biomass
Chemical composition and the stability of bio-oil are closely related to the quality of biomass materials used (i.e. type, initial moisture, composition, and mineral constituents, etc.) as well as the pyrolysis conditions of the biomass (i.e. pyrolysis temperature, retention time, gaseous phase, heating rate, and particle sizes). In-depth research into the pyrolysis mechanism of biomass is essential to understand and control the generation channels of bio-oil. Once this is achieved, sound storage stability of bio-oil will be possible.
(2) Application standards of bio-oil
Bio-oil can be used as liquid fuels and chemical materials. Obviously, different usages have different demands on bio-oil stability. The testing of storage stability of bio-oil and applications of bio-oil should be standardized and normalized, thereby guiding the research of stability.
(3) Economical efficiency
Most methods to improve bio-oil stability require consuming expensive chemicals, such as catalysts, hydrogen gas, and emulgator. They also must consume a certain amount of energy. Due to these facts, the yield of refined bio-oil is reduced to varying degrees. Hence, it is vital that the selection of methods used to improve bio-oil stability consider the economical efficiency.

7. Conclusions

Bio-oil has several advantages, such as availability of raw materials, renewability, ease of transportations, and a high energy density. It is a key clean fuel and can potentially be used as a chemical material. But the components of bio-oil contain a large portion of unsaturated bonds (such as C=C, C=O, etc.), which tend to undergo internal reactions during storage, such as polymerization, condensation, esterization, and oxidation. These bonds and the aging reactions are responsible for the poor storage and thermal stability of bio-oil. As of now, bio-oil cannot replace traditional fossil fuels in its current quality, stability, and production cost.

The storage temperature, storage time, oxygen and aging reactions have notable effects on bio-oil stability. Various methods have been proposed to improve bio-oil stability. The primary methods for refining bio-oil include catalytic cracking, catalytic hydrogenation, and catalytic esterification. The core technology of all chemical refining methods is the selection of catalysts.

Advances in fast pyrolysis and bio-oil updating technologies will enable bio-oil to be highlighted as a renewable clean fuel. In the long run, the key to improving the quality of bio-oil is to further understand the mechanism of the biomass fast pyrolysis and to prepare quality bio-oil through selective pyrolysis. A series of bio-oil testing and application standards are needed to promote the industrial applications of bio-oil.

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